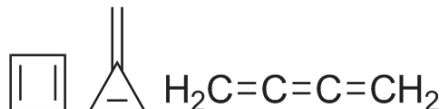# Homework 10 Answer Key

December 5, 2014

1 Question 1

Draw the three isomers of C_4H_4 with two double bonds. Calculate the total Huckel energies for each isomer and predict their relative stability.

$$H_2C=C=C=CH_2$$

For cyclobutadiene, left: $\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$ where $x = \frac{\alpha - E}{\beta}$.

With energies of $\alpha + 2\beta$, α and $\alpha - 2\beta$ and 4 electrons means E= $4\alpha + 4\beta$.

For methylcyclopropene, center: $\begin{vmatrix} x & 1 & 1 & 0 \\ 1 & x & 1 & 0 \\ 1 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$ where $x = \frac{\alpha - E}{\beta}$.

With energies of $\alpha - 1.49\beta$, $\alpha - \beta$, $\alpha + 0.31\beta$, and $\alpha + 2.17\beta$ and 4 π electrons means E= $4\alpha + 4.96\beta$.

For allene, right: $\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$ where $x = \frac{\alpha - E}{\beta}$.

With energies of $\alpha \pm 1.62\beta$ and $\alpha \pm 0.62\beta$ and 6 electrons means E= $6\alpha + 3.24\beta$.

Relative stability: Allene ¿ cyclobutadiene ¿ methylcylopropene.

2 P. 13.9

Predict which of the bent molecules, BH_2 or NH_2, should have the larger bond angle on the basis of the Walsh correlation diagram in Figure 24.11. Explain your answer.

Molecule:	BH_2	NH_2
Valence e^-:	5	7
HOMO:	$2a_1$	$1b_1$

Both molecules are equivalent through the $(2a_1)^1$ orbital. However, by adding the second electron to the $2a_1$ orbital and the electron to the $1b_1$ orbital, the NH_2 molecule is shifted more to the bent form to lower the energy. Thus, the BH_2 molecule has the larger bond angle.

3   P 13.18

The occupied MOs of ethene are shown next along with the MO energies. Indicate which AOs are most important in each MO and indicate the relative phases of the AOs. Classify the MOs as localized or delocalized, σ or π bonds, and bonding, nonbonding or antibonding. Image shown on next page

The MOs corresponding to the energies -303.56 eV and -303.51 eV are the in-phase and out-of-phase combinations of the 1s AOs on C. They are localized and nonbonding. The MO corresponding to -28.3 eV is the in-phase combination of the 2s AO on C with the 1s AOs on H. It is a delocalized σ bonding MO. The next four MOs in order of increasing energy involve σ bonding in the molecular skeleton. The C AOs are sp^2 hybrids and the H AOs are $1s$. These four MOs differ in the orientation of the sp^2 hybrid AOs on C and the relative phases of the sp^2 hybrid AOs on C and the H $1s$ AOs. The MO corresponding to -21.6 eV is the out-of-phase combination of the two CH_2 groups in which in-phase bonding of the C and H AOs occurs. It is a delocalzed bonding MO in the C–H regions and is antibonding in the C–C region. The MO corresponding to -16.1 eV arises from an in-phase combination of the sp^2 hybrid along the C–C bond with the H$1s$ AOs. It is a delocalized bonding MO in the C–H regions and is bonding (no node through the bond) in the C–C region. Two sp^2 hybrids on C can be combined to give a resultant sp^2 hybrid oriented perpendicular to the C–C bond on each C. The in-phase combinations of these AOs with the H $1s$ AOs results in the MO corresponding to -17.6 eV. It is a delocalized bonding MO in the C–H regions but is nonbonding in the C–C region. The out-of-phase combination results in the MO corresponding to -13.8 eV. The MO corresponding to -10.3 eV arises from an in-phase combination of the C $2p$ AOs perpendicular to the molecular plane. It is a delocalized bonding MO of π symmetry.

2
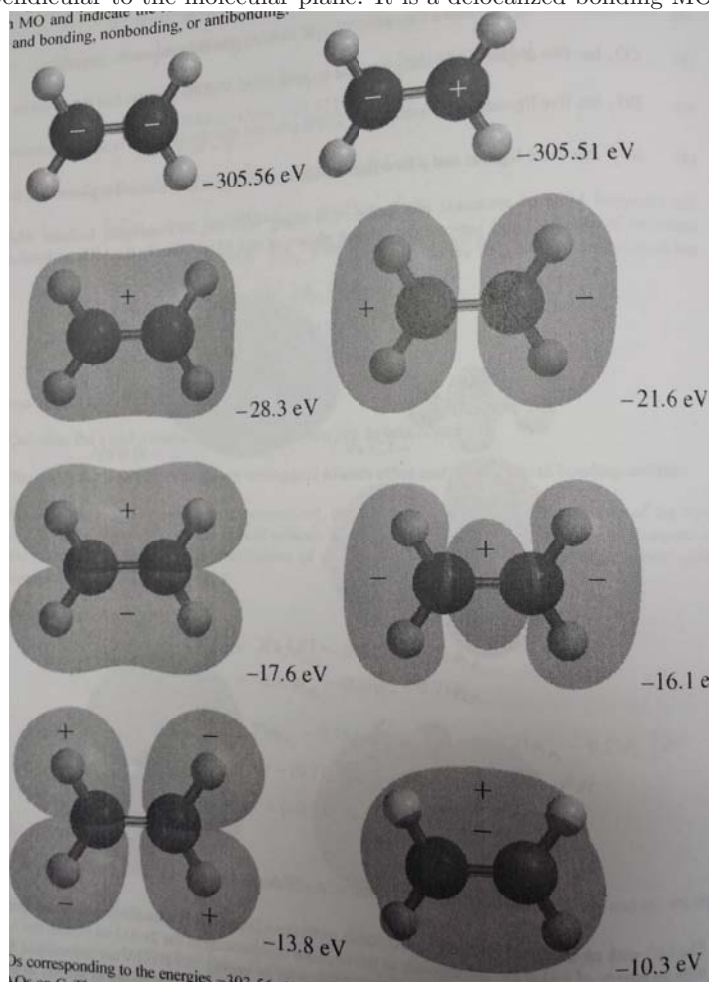
4   P 13.21

Determine the AO coefficients for the lowest energy Hückel π MO for butadiene.

The energy is given by $\epsilon = \alpha + 1.618\beta$ and $\psi_\pi = \psi^a_{2p_z} + \psi^b_{2p_z} + \psi^c_{2p_z} + \psi^d_{2p_z}$. Thus, the secular equations are:

$$(1): c_1(H_{aa} - \epsilon S_{aa}) + c_2(H_{ab} - \epsilon S_{ab}) + c_3(H_{ac} - \epsilon S_{ac}) + c_4(H_{ad} - \epsilon S_{ad}) = 0$$

$$(2): c_1(H_{ba} - \epsilon S_{ba}) + c_2(H_{bb} - \epsilon S_{bb}) + c_3(H_{bc} - \epsilon S_{bc}) + c_4(H_{bd} - \epsilon S_{bd}) = 0$$

$$(3): c_1(H_{ca} - \epsilon S_{ca}) + c_2(H_{cb} - \epsilon S_{cb}) + c_3(H_{cc} - \epsilon S_{cc}) + c_4(H_{cd} - \epsilon S_{cd}) = 0$$

$$(4): c_1(H_{da} - \epsilon S_{da}) + c_2(H_{db} - \epsilon S_{db}) + c_3(H_{dc} - \epsilon S_{dc}) + c_4(H_{dd} - \epsilon S_{dd}) = 0$$

The overlap is given by $S_{jk} = \sigma_{jk}$ and we assign values to the H_{jk} as follows:

$$H_{jk} = \begin{cases} \alpha \text{ if } j = k \\ \beta \text{ if } j \text{ and } k \text{ differ by 1, and} \\ 0 \text{ otherwise} \end{cases}$$

Substituting in the four secular equations gives the following relations:

(1) $c_1[\alpha - (\alpha + 1.62\beta)] + c_2[\beta] = 0$

We conclude that $c_2 = 1.62c_1$.

(2) $c_1\beta + c_2[\alpha - (\alpha + 1.62\beta)] + c_3\beta = 0$

We conclude that $c_1 + c_3 = 1.62c_2$ or $c_3 = (1.62^2 - 1)c_1$.

(3) $c_2\beta + c_3[\alpha - (\alpha + 1.62\beta)] + c_4\beta = 0$

We conclude that $c_2 + c_4 = 1.62c_3$ or $c_4 = \dfrac{(1.62^2 - 1)}{1.62}c_1$.

The fourth equation needed to solve this system is the normalization condition, defined by

$$1 = \int (\psi_\pi)^* \psi_\pi \, d\tau = \int (\psi^a_{2p_z} + \psi^b_{2p_z} + \psi^c_{2p_z} + \psi^d_{2p_z})^2 \, d\tau$$

$$= c_1^2 \int (\psi^a_{2p_z})^2 \, d\tau + c_2^2 \int (\psi^b_{2p_z})^2 \, d\tau + c_3^2 \int (\psi^c_{2p_z})^2 \, d\tau + c_4^2 \int (\psi^d_{2p_z})^2 \, d\tau$$

$$+ 2c_1c_2 \int \psi^a_{2p_z} \psi^b_{2p_z} \, d\tau + 2c_1c_3 \int \psi^a_{2p_z} \psi^c_{2p_z} \, d\tau + 2c_1c_4 \int \psi^a_{2p_z} \psi^d_{2p_z} \, d\tau$$

$$+ 2c_2c_3 \int \psi^b_{2p_z} \psi^c_{2p_z} \, d\tau + 2c_2c_4 \int \psi^b_{2p_z} \psi^d_{2p_z} \, d\tau$$

$$= c_1^2 + c_2^2 + c_3^2 + c_4^2 + 2c_1c_2 S_{ab} + 2c_1c_3 S_{ac} + 2c_1c_4 S_{ad} + 2c_2c_3 S_{bc} + 2c_2c_4 S_{bd}$$
$$= c_1^2 + c_2^2 + c_3^2 + c_4^2$$

Substituting 1-3 into the normalization equation yields

$$c_1^2 + 1.62^2 c_1^2 + (1.62^2 - 1)^2 c_1^2 + \left[\frac{(1.62^2 - 1)}{1.62}\right]^2 c_1^2 = 1$$

or

$$c_1^2 = \frac{1}{1 + 1.62^2 + (1.62^2 - 1)^2 + \left[\frac{(1.62^2 - 1)}{1.62}\right]^2}$$

and

$$c_1 = 0.3717$$
$$c_2 = 0.6015$$
$$c_3 = 0.6015$$
$$c_4 = 0.3717$$
$$\psi_\pi = 0.3717\psi^a_{2p_z} + 0.6015\psi^b_{2p_z} + 0.6015\psi^c_{2p_z} + 0.3717\psi^d_{2p_z}$$

5   P 13.30

The energies of three occupied orbitals (the a_2 HOMO and doubly degenerate e orbitals) are shown. The energy of the unoccupied LUMO is also shown. The angle on the abcissa is the F–B–F bond angle. Based on the MO diagram, is boron trifluoride planar or pyramidal? Which structure does VSEPR model predict?

BF$_3$ has 32 electrons, which fill up through MOs 14, 15, and 16. Because the MO energies all decrease as the F–B–F bond angle approaches 120°, BF$_3$ is a planar molecule.

The VSEPR model also predicts a trigonal planar geometry since this minimizes the electron pair repulsion.